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(54) Title: REACTIVE POLYMERS HAVING PENDANT FLEXIBLE SIDE CHAINS PREPARED FROM ETHYLENICALLY UNSATURATED ISOCYANATES (57) Abstract This invention relates to reactive polymers, e.g., aqueous emulsion polymers, having pendant flexible or dangling side chains prepared from ethylenically unsaturated isocyanates. The reactive polymers contain ethylenic unsaturation near the surface or in the surface area of the particles that form the polymers, the ethylenic unsaturation being connected to the polymer through the pendant flexible or dangling side chains. This invention also relates to the process for preparing the reactive polymers, to cross-linkable formulations based on the reactive polymers, and to thermoplastic and cross-linked films prepared from the reactive polymers. The reactive polymers are useful as decorative and functional coatings, inks, adhesives, textile coatings and sealants.		

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**REACTIVE POLYMERS HAVING PENDANT FLEXIBLE
SIDE CHAINS PREPARED FROM ETHYLENICALLY
UNSATURATED ISOCYANATES**

Related Applications

The following are related, commonly assigned applications, filed on an even date herewith:

U.S. Patent Application Serial No. (D-16894); U.S. Patent Application Serial No. (D-16967); U.S. Patent Application Serial No. (D-17136); all of which are incorporated herein by reference.

Brief Summary of the Invention

Technical Field

This invention relates to reactive polymers, e.g., aqueous emulsion polymers, having pendant flexible or dangling side chains prepared from ethylenically unsaturated isocyanates. The reactive polymers contain ethylenic unsaturation near the surface or in the surface area of the particles that form the polymers, the ethylenic unsaturation being connected to the polymer through the pendant flexible or dangling side chains. This invention also relates to the process for preparing the reactive polymers, to crosslinkable formulations based on the reactive polymers, and to thermoplastic and crosslinked films prepared from the reactive polymers. The reactive polymers are useful as decorative and functional coatings, inks, adhesives, textile coatings and sealants.

Background of the Invention

Aqueous emulsion polymers or latexes in both clear and pigmented form are well-known, widely-used articles of commerce. Examples of these uses include interior and exterior architectural coatings, general metal coatings, adhesives, and the like. The latexes are formed by aqueous emulsion polymerization of monoethylenically

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unsaturated monomers as styrene, butyl acrylate, methyl methacrylate, vinyl acetate, acrylic acid, glycidyl acrylate, 2-hydroxyethyl acrylate, and similar compounds. When ethylenically unsaturated monomers that contain a functionality other than unsaturation, such as the carboxyl group in acrylic acid, and the hydroxyl group in 2-hydroxyethyl acrylate, are used, there is a propensity for these groups to be found at or near the surface of the emulsion particles because of the affinity of the groups for the aqueous environment. In addition, techniques for increasing the amount of any non-water reactive functional group near the surface of the emulsion particles are known to those skilled in the art of emulsion polymerization. Illustrative of such techniques is the production of a core and shell latex in which the core of the particles has a given composition that may contain a small amount of the functional groups or be devoid of them and the shell or outer layers of the particle have a different composition which may be rich in the functional groups, and the like.

There is a need for products that have improved, lower initial molecular weight characteristics, improved adhesion, and products that will crosslink under ambient conditions or low to moderate temperatures in the presence of air.

Disclosure of the Invention

This invention relates in part to a polymer having one or more pendant flexible side chains connected thereto, wherein said pendant flexible side chains contain ethylenic unsaturation and are connected to said polymer by a urethane linkage, said urethane linkage formed by the reaction of an ethylenically unsaturated isocyanate with a hydroxyl group on said polymer.

This invention also relates in part to a process for preparing a polymer having one or more pendant flexible side chains connected thereto comprising:

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- (a) preparing a precursor polymer having hydroxyl group functionality from one or more ethylenically unsaturated monomers;
- (b) post reacting the precursor polymer with one or more ethylenically unsaturated isocyanates; and
- (c) optionally recovering the step (b) polymer and redissolving it in an organic solvent.

It has been found that ethylenic unsaturation of various types can be formed on, in, or near the surface of polymer particles that contain free, reactive hydroxyl functionality by first preparing a precursor polymer and then post reacting it with one or more suitable ethylenically unsaturated isocyanates containing a functional group that will react with all or a portion of the free, reactive hydroxyl functionality on the precursor polymer particle. The post reactant will contain an ethylenic unsaturation group that can air dry or force dry into a crosslinked, solvent resistant coating with broad utility characteristics. Air dry means to cure the liquid coating into a solid film by allowing it to remain under ambient conditions for a period of time sufficient to effect solidification. Force dry means to cure the liquid coating into a solid film by exposing it to a thermal source such as an oven, to an actinic radiation source such as ultraviolet light, as electron beams, as lasers, and the like with or without a predrying step under ambient conditions to remove water, solvent, or other carrier. For purposes of this invention, ethylenic unsaturation shall include all permissible compounds, groups or substituents having at least one carbon-carbon double bond including, for example, (meth)acrylates, vinyls, allyls, alkenes and the like.

In an embodiment of this invention, the post modified polymer containing ethylenic unsaturation is recovered from the aqueous environment, dissolved in an organic solvent, and applied to a substrate to effect air-cure crosslinking. In specific embodiments of this invention, the water-borne polymer particles can be crosslinked with free radicals generated from an actinic energy source such as an electron beam or by formulation with a free radical-generating

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photoinitiator and, if necessary, a synergist, and exposed to an ultraviolet light source such as sunlight, mercury vapor lamps, xenon lamps, etc.

In another embodiment of the invention, the polymer precursor containing free, reactive hydroxyl functionality can be recovered from the aqueous media and dissolved in an organic solvent or can be prepared in an organic solvent. The polymer in organic solvent can be modified by post reaction with one or more of the above described reactants for aqueous systems to form a polymer with pendant flexible chains having ethylenic unsaturation connected thereto that can be crosslinked under ambient, air-cure conditions or radiation-cure conditions.

In a further embodiment of the invention, the post modified polymers containing ethylenic unsaturation neat or formulated with photoinitiator and/or other radiation-reactive chemicals is recovered as a solid, uncrosslinked film by removal of either the aqueous or organic solvent media. The solid film is then used as a photoresist in the manufacture of printed circuit boards or other article by selective exposure to radiation. Selective exposure is provided by a mask through which radiation does not penetrate.

The reactive polymers of the invention can be used in a variety of ways including but not limited to clear, colored, filled, or pigmented crosslinked latexes, water-borne alkyds, solvent-borne alkyds, radiation curable systems, and the like. Illustrative of generalized utility areas are coatings for metal, paper, plastics, wood, and masonry; inks; adhesives; binding agents for concrete; photoresists; and the like. Among the specific coating end uses that can be mentioned are interior and exterior architectural coatings, can coatings, office and home furniture coatings, pipeline coatings, sign coatings, maintenance coatings, business machine coatings, functional and decorative automotive coatings, textile coatings, conformal coatings, electrical and electronic coatings and the like.

Detailed Description

Hydroxyl group functionalized polymer particles can be reacted with one or more ethylenically unsaturated isocyanates, in which the reaction takes place with a hydroxyl group to form a free ethylenically unsaturated terminated, pendant flexible side chain connected to the polymer particle through a urethane linkage. For purposes of this invention, the term "urethane linkage" is contemplated to include all permissible linkages resulting from the reaction of an ethylenically unsaturated isocyanate with a hydroxyl group on the polymer which links an ethylenically unsaturated terminated, pendant flexible side chain to the polymer.

The polymers having hydroxyl functionality can be prepared from a variety of monoethylenically unsaturated monomers including, for example, acrylates and methacrylates (both referred to herein as (meth)acrylates); vinyl esters; vinyl aromatic, cycloaliphatic, and heterocycles; hydroxyalkyl (meth)acrylates and their derivatives; vinyl halogens and vinylidene halogens; alkenes and substituted alkenes; nitriles; and vinyl ethers. If desired, minor amounts of di- or triethylenically unsaturated monomers can be used if they do not unduly interfere with the polymerization process by causing excessive crosslinking and unusable polymer formation. Illustrative of the (meth)acrylates are methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylates, butyl (meth)acrylates, pentyl (meth)acrylates, hexyl (meth)acrylates, heptyl (meth)acrylates, octyl (meth)acrylates, nonyl (meth)acrylates, decyl (meth)acrylates, (meth)acrylic acid, and the like. Illustrative of the vinyl esters are vinyl acetate, vinyl propionates, vinyl butyrates, vinyl pivalates, vinyl hexanoates, vinyl heptanoates, vinyl octanoates, vinyl isovalerate, vinyl 2-ethylhexanoate, vinyl benzoates, vinyl crotonate, vinyl laurates, vinyl myristate, vinyl linoleate, vinyl linolenate, vinyl cinnamate, vinyl stearates, vinyl oleate, vinyl naphthanoates, vinyl cyclopentanoates, vinyl versatates, vinyl salicylate, monovinyl adducts of difunctional or higher functional carboxylic acids as monovinyl adipate, and the like. Illustrative of the vinyl aromatic, cycloaliphatic, and heterocycles are styrene, vinyl

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cyclohexane, vinyl cyclopentane, vinyl toluene, vinyl anthracenes, 3-vinyl benzyl chloride, 4-vinyl biphenyl, 4-vinyl-1-cyclohexene, vinyl cyclooctane, 2-vinyl naphthalene, 5-vinyl-2-norbornene, 1-vinyl imidazole, 2-vinyl pyridine, 4-vinyl pyridine, 1-vinyl-2-pyrrolidinone, 9-vinyl carbazole, 3-vinylbenzyl chloride, and the like. The hydroxyalkyl (meth)acrylates and their derivatives include 2-hydroxyethyl acrylate (HEA), hydroxypropyl acrylate (HPA), ethylene oxide and propylene derivatives of HEA and HPA containing from 1 to about 20 moles of the alkylene oxide, caprolactone (meth)acrylates which are epsilon-caprolactone derivatives of HEA and HPA containing from 1 to about 6 moles of epsilon-caprolactone, carboxylic acid terminated adducts of HEA and HPA and the alkylene oxide and caprolactone derivatives of HEA and HPA, and the like. Illustrative of the vinyl halogens and vinylidene halogens are vinyl chloride, vinylidene chloride, vinyl fluoride, vinylidene fluoride, and the like. Illustrative of the alkenes and substituted alkenes are ethylene, propylene, butenes, pentenes, hexenes, heptenes, octenes, nonenes, decenes, 4-chloro-1-butene, 4, 6-dichloro-1-hexene, 5-fluoro-2-hexene, and the like. Illustrative of the nitriles are acrylonitrile, methacrylonitrile, and the like. Illustrative of the vinyl ethers are methyl vinyl ether, ethyl vinyl ether, propyl vinyl ethers, butyl vinyl ethers, pentyl vinyl ethers, hexyl vinyl ethers, heptyl vinyl ethers, octyl vinyl ethers, 2-methyl-1-butyl vinyl ether, and the like. Various carboxylic acid monomers can be used, such as acrylic acid, methacrylic acid, ethacrylic acid, alpha-chloroacrylic acid, crotonic acid, fumaric acid, citraconic acid, mesaconic acid, itaconic acid, maleic acid and the like including mixtures thereof.

The polymers are prepared by conventional techniques as exemplified herein and as are known to those skilled in the art of polymerization. The molecular weight of the copolymers making up the polymer particles can vary over wide ranges of average molecular weight and can have number-average molecular weights of from about 1000 to about 1,000,000 or more with a distribution of molecular weights existing. Since film formation of aqueous emulsion polymers conventionally takes place by particle coalescence in which the outer

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regions of the particles come together and interact to form the final film, it is preferable that the polymer particles of this invention contain a major quantity of the functional groups in, at or near the surface (i.e., the surface region) of the particles, though it is realized that some of the functional groups may be positioned within the interior of the particles. Although the number of copolymers in each polymer particle is indeterminate since particle size and copolymer molecular weight will vary, it is important that, on the average, hydroxyl functionality exist on a majority of any copolymer molecules and that at least some of the functionality be found in the surface region or related region so it can react with the post reaction reactants. Other functional groups such as carboxyl, amine, etc., may also be present in the hydroxyl functional polymers, i.e., precursor polymers, used in this invention.

Illustrative of the ethylenically unsaturated isocyanates that can be used to react with the precursor polymer particles to produce the reactive polymers of this invention are the isocyanato alkyl (meth)acrylates such as 2-isocyanatoethyl methacrylate, 3-isocyanatopropyl methacrylate, and the like; the monoisocyanates prepared from diolefins such as the dialkylidene aryls that produce compounds such as 1-(1-isocyanato-1-methyl ethyl)-3-(1-methyl ethenyl) benzene (p-TMI), 1-(1-isocyanato-1-methyl ethyl)-4-(1-methyl ethenyl) benzene (m-TMI), 1-(1-isocyanato-1-methyl propyl)-3-(1-methyl propenyl) benzene, 1-(1-isocyanato-1-methyl propyl)-4-(1-methyl propenyl) benzene, 1-(1-isocyanato-1-methyl propyl)-4-(1-methyl ethenyl) benzene, 1-(1-isocyanato-1-ethyl)-3-(1-ethenyl) benzene, 1-(1-isocyanato-1-ethyl)-4-(1-ethenyl) benzene, and the like. Methods for manufacture of such isocyanates can be found in U. S. Patent 2,718,516, U. S. Patent 2,821,544, U. S. Patent 4,377,530 and U. S. Patent 4,439,616 and certain of the isocyanates are commercially available. Mixtures of the various ethylenically unsaturated isocyanates may be used for purposes of this invention. Both substituted and unsubstituted ethylenically unsaturated isocyanates may be used for purposes of this invention.

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In an embodiment of this invention, initial aqueous emulsions used to prepare the aqueous emulsion polymers of this invention have an initial pH of about 2.0 to 10.5 and contain about 0.05 to 20% or more of hydroxyl functionality, preferably an initial pH of 3.5 to 9.0 and contain from about 0.1% to 15% hydroxyl functionality, and are prepared at about 40°C to about 100°C for about 6 to 48 hours, preferably at about 60°C to about 90°C for about 10 to about 24 hours under atmospheric pressure or superatmospheric pressure of about 15 psig to about 100 psig.

The post reaction leading to the reactive polymers of this invention are carried out at a temperature of from about 0°C to about 100°C, preferably from about 20°C to about 90°C, for about 30 minutes to 24 hours or more under atmospheric or superatmospheric pressure of about 15 psig to about 100 psig.

Although not essential, a stoichiometric deficiency of the ethylenically unsaturated isocyanate may be employed in order to leave some hydroxyl functionality in the polymer. Excess isocyanate is generally avoided since it introduces residual unpolymerized monomer which is undesirable. At least about 0.5% of the ethylenically unsaturated isocyanate, based on the weight of the polymer, is used. Based on the hydroxyl content of the precursor polymer, it is preferred to consume at least 5%, preferably from 10% to about 90%, of the hydroxyl functionality by reaction with the ethylenically unsaturated isocyanate.

As indicated above, other functional groups such as carboxyl, amine, etc., may be present in the hydroxyl functional polymers, i.e., precursor polymers, used in this invention. Other permissible post reactions may be carried out in a sequential manner so there is no adverse interaction of the reactants used for the post reaction of this invention. Illustrative of other such post reactions include, for example, (1) reaction with a carbodiimide (meth)acrylate wherein reaction takes place with carboxyl groups on the precursor polymer particle; (2) reaction with an imine to form amine groups on the precursor polymer particle and then with an ethylenically

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unsaturated isocyanate wherein reaction takes place with the amine groups to form free vinyl groups connected to the particle with urea linkages; (3) reaction with an imine to form amine groups on the precursor polymer particle and then with either a mixture or a sequence of glycidyl (meth)acrylate and a carbodiimide (meth)acrylate; and the like. Both substituted and unsubstituted post reactants may be used for purposes of this invention. Suitable other post reactions which may be employed herein include those disclosed in U.S. Patent Application Serial No. (D-16967), U.S. Patent Application Serial No. (D-16894) and U.S. Patent Application Serial No. (D-17136), all of which are incorporated herein by reference. This invention is not intended to be limited in any manner by the number or combination of permissible post reactions.

The reactive polymers, e.g., aqueous emulsion polymers, of this invention can be used in a variety of ways illustrative of which are as air-dry coatings that will increase in molecular weight presumably through crosslinking by reaction with atmospheric oxygen and/or incidental radiation under ambient conditions without the use of heavy metal catalysts known as drier salts, though such catalysts may be optionally included in coating formulations if desired; as thermally crosslinkable coatings when formulated with peroxides that will break down and cause crosslinking to take place through the ethylenic unsaturation; as radiation curable coatings, preferably in the presence of free-radical generating photoinitiators of either the homolytic fragmentation type or the hydrogen abstraction type which are usually used in combination with a nitrogen-containing synergist when ultraviolet light is used as the radiation source; as solvent reduced coatings in which relatively large quantities of solvent, i.e., more than flexibilizing or plasticizing quantities, are added to the formulation before application to a substrate; and the like.

The reactive polymers of this invention may be used alone or in combination with other systems illustrative of which are aqueous emulsions, water reducible alkyds, solutions of polymers, radiation-curable (meth)acrylates or epoxides, unsaturated fatty acid derivatives,

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linseed oil, soybean oil, tall oil, and the like. In an embodiment of this invention, aqueous alkyds having molecular weights of from about 500 to 5000 are prepared by adding chain transfer agents to the emulsion polymers during polymerization. In another embodiment of this invention, the reactive polymers of this invention are recovered as a solid, redissolved in an organic solvent, and formulated into solvent-borne coatings, particularly high solids alkyd coatings when low molecular weight polymers are formed in the emulsion process. Suitable solvents are polar in nature illustrative of which are esters, ketones, esters of lactic acid; ethylene oxide glycol ethers as ethylene glycol monomethyl ether, ethylene glycol and diethylene glycol monoethyl ethers, ethylene glycol and diethylene glycol monopropyl ethers, ethylene glycol and diethylene glycol monobutyl ethers, and ethylene glycol and diethylene glycol monohexyl ethers; propylene oxide glycol ethers such as propylene glycol and dipropylene glycol monomethyl ethers, propylene glycol and dipropylene glycol monopropyl ethers, propylene glycol and dipropylene glycol monobutyl ethers, propylene glycol monobutyloxyethyl ether; toluene, methyl ethyl ketone, xylene, dimethylformamide, ethyl acetate, butyl acetate, tetrahydrofuran, 1,1,1-trichloroethane, cyclohexanone, hydroxyethers, and the like. If desired, these solvents may be used in combination with aliphatic hydrocarbons, aromatic hydrocarbons, super critical carbon dioxide, and the like.

When polymers with glass transition temperatures greater than room temperature are formed, film forming agents or plasticizers of various types may be incorporated into the formulations. Such plasticizers may be (1) of a nonreactive nature, illustrative of which are the various esters, ketones, hydroxyethers, and the like which may be fugitive in nature when they have low molecular weight and are lost via evaporation or may be retained by the dry film when they have relatively high molecular weight; (2) of a reactive nature and contain ethylenic unsaturation which reacts with the unsaturation in the polymers of the invention and thus become incorporated into the final film, illustrative of which are diethylene glycol diacrylate,

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ethylene glycol diacrylate, divinyl adipate, diisopropenyl adipate, divinyl succinate, vinyl crotonate, diallyl phthalate, urethane acrylates, acrylated epoxides, trimethylol propane triacrylate, pentaerythritol triacrylate and tetraacrylate, and the like; or (3) a mixture of nonreactive and reactive plasticizers.

Optional heavy metal driers that may be incorporated into the coatings to promote curing. These driers are metal salts of organic acids illustrative of which acids are tall oil fatty acids, ethylhexanoic acid, neodecanoic acids, naphthenic acids, and the like. Illustrative of typical metals used for air- or ambient-dry systems are cobalt, zirconium, and manganese, and the like, and for heat-cure coatings are iron, manganese, cobalt, cerium, and the like. Auxiliary driers include lead, barium, calcium, zirconyl (ZrO_2), zinc, and the like. If desired, mixtures of the various driers can be used.

Illustrative of the peroxides or compounds that will generate oxygen when heated that can be used in the thermally curable coating compositions of this invention are benzoyl peroxide, t-butyl peroxybenzoate, diisopropyl peroxide, and the like. These compounds are used in an amount of about 0.05% to about 5%, preferably from about 0.1% to about 2.5%. It is known to those skilled in the art of these compounds that the cure temperature and decomposition temperature of any chosen compound must be properly considered when they are used.

Illustrative of the homolytic fragmentation-type photoinitiators used in the photocurable coating compositions are 2,2-diethoxyacetophenone, 2,2-dimethoxy-2-phenylacetophenone, 1-hydroxycyclohexylphenyl ketone, acetophenone, and the like. Illustrative of the hydrogen abstraction-type photoinitiators are benzophenone, benzophenone derivatives, 2-chlorothioxanthone, isopropylthioxanthone, fluorenone, benzil, 9,10-anthraquinone, camphor quinones, 1,3,5-triacetylbenzene, 3-ketocoumarines, acridone, bis-(4,4'-dimethylamino)benzophenone, and the like. Illustrative of the synergists useful in combination with the hydrogen abstraction-type photoinitiators are amine, amides, urethanes or ureas with a

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hydrogen-bearing carbon atom in the alpha position to the nitrogen group among which one can mention dimethylethanol amine, triethyl amine; primary, secondary, and tertiary amine-terminated poly(propylene oxide) polyols as well urea and urethane derivatives of such polyols, and the like.

Although many of the reactive polymers of this invention can be cured alone with or without added photoinitiator when exposed to ultraviolet light, they may be combined with one or more other radiation-polymerizable ethylenically unsaturated compounds such as substituted or unsubstituted (meth)acrylates. Illustrative of the (meth)acrylates suitable for use in the radiation curable compositions of the invention are the esters of (meth)acrylic acid with monohydric and polyhydric compounds among which one can mention ethyl, butyl, hexyl, octyl, decyl, and the like (meth)acrylates; neopentyl (meth)acrylate, trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate and tetra(meth)acrylate, caprolactone (meth)acrylates which are adducts of 1 to 10 moles of epsilon-caprolactone and a hydroxylalkyl (meth)acrylate, alkoxylated (meth)acrylates, glycerol (meth)acrylates, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 2,2-dimethyl-3-hydroxypropyl-2,2-dimethyl-3-hydroxypropionate di(meth)acrylate, isobornyl (meth)acrylate, tripropylene glycol di(meth)acrylate, unsaturated polyesters, 2,2-dimethyl-3-hydroxypropyl-2,2-dimethyl-3-hydroxypropionate di(meth)acrylates as well as alkoxylated versions of such di(meth)acrylates, urethane (meth)acrylates, (meth)acrylated epoxides, (meth)acrylated linseed oil, (meth)acrylated soybean oil, (meth)acrylated polybutadiene, and the like. In addition, the formulations may contain N-vinyl pyrrolidone, divinylbenzene, and the like.

The reactive polymers, e.g., aqueous emulsions, of this invention can be formulated with a variety of vinyl esters alone or in combination with other radiation-polymerizable ethylenically-unsaturated compounds in the photocurable compositions of this invention. Illustrative of the vinyl esters are vinyl 2-ethylhexanoate,

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vinyl benzoate, vinyl isovalerate, vinyl nonylates, vinyl neononanoate, vinyl neodecanoate, vinyl myristate, vinyl oleate, vinyl linoleate, vinyl abietate, divinyl adipate, divinyl oxalate, divinyl succinate, divinyl fumarate, divinyl maleate, diisopropenyl adipate, trivinyl mellitate, trivinyl citrate, 1, 2, 4-trivinyl benzenetricarboxylate, tetravinyl mellophanate, 3,3',4,4'-tetravinyl benzophenonetetracarboxylate, and the like. Such vinyl ester can also be used as reactive flexibilizers/plasticizers in other non-photocurable coating compositions of the invention.

The photopolymerization is carried out by exposing the uncured film or coating to light radiation which is rich in short wave radiation. Particularly useful is radiation of about 200 to 450 nanometers in wavelength. Illustrative of appropriate light sources are low-pressure, medium pressure, and high-pressure mercury vapor lamps as well as lamps of this type that have been doped to exclude selected wavelengths; xenon and other flash-type lamps; lasers operating in the above listed wavelength range; sunlight, and the like. Other sources of radiant energy such as electron beams, gamma radiation, X-rays, and so on can also be used.

Any permissible conventional additives, processing aids, etc. may be employed in conventional amounts in the compositions and processes of this invention. This invention is not intended to be limited in any manner by any permissible additives, processing aids, and the like.

The coating compositions of the invention are applied to appropriate substrates as thin films by a variety of processes illustrative of which are roll coating, dip coating, spray coating, brushing, flexographic, lithographic, and offset-web printing processes, and the like.

As used herein, the term "substituted" is contemplated to include all permissible substituents of organic compounds unless otherwise indicated. In a broad aspect, the permissible substituents include acyclic and cyclic, branched and unbranched, carbocyclic and heterocyclic, aromatic and nonaromatic substituents of organic

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compounds. Illustrative substituents include, for example, alkyl, alkyloxy, aryl, aryloxy, hydroxy, hydroxyalkyl, amino, aminoalkyl, halogen and the like in which the number of carbons can range from 1 to about 20 or more, preferably from 1 to about 12. The permissible substituents can be one or more and the same or different for appropriate organic compounds. This invention is not intended to be limited in any manner by the permissible substituents of organic compounds.

The invention is illustrated by certain of the following examples.

Glossary of Terms and Compounds

Gel Fraction - The gel fraction or gel content is the amount of material that is insoluble when a given mass of the cured coating is extracted with tetrahydrofuran (THF) for 18 hours at room temperature. The extracted film is removed from the THF, rinsed with fresh THF, and dried at 110°C for one hour. The gel fraction, expressed as a percentage, is calculated with the following expression.

$$\text{Gel Fraction} = (1 - ((\text{Weight of original film} - \text{Weight extracted film}) / (\text{Weight of original film}))) \times (100\%)$$

Gloss, 60° -- ASTM D 523

Gloss, 20° -- ASTM D 523

Yellowness Index -- ASTM D 1925

Crosshatch Adhesion -- ASTM D 3359

Impact, Forward/Reverse -- ASTM D-2794

Definition of Image, DOI -- measurement of the light image reflected off a surface using a commercially available DOI instrument.

Surfactant 1 - A sodium dioctyl sulfosuccinate anionic surfactant commercially available from American Cyanamid Company under the designation Aerosol® OT-75.

Surfactant 2 - A 70% solution of nonyl phenol-based alkylene oxide nonionic surfactant in water commercially available

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from Union Carbide Chemicals and Plastics Company Inc. under the designation Tergitol® NP-40.

Examples

Preparation A

Preparation of an aqueous emulsion polymer

A monomer solution mixture composed of the compounds in Table 1 was prepared.

Table 1

<u>Monomer</u>	<u>Grams Used</u>	<u>Wt. % of Mixture</u>
Methyl methacrylate	450.0	44.2
Styrene	200.0	19.7
n-Butyl methacrylate	250.0	24.6
Methacrylic acid	100.0	9.8
Mercaptoacetic acid	17.2	1.7

A glass resin kettle equipped for temperature control and agitation was charged with 1,100.0 grams of deionized water, 0.34 gram of Surfactant 1, 1.30 grams of Surfactant 2, and 50 grams of the monomer solution. A nitrogen purge was started in the reaction mixture, and the contents of the resin kettle were increased to 85°C at which point an initiator mixture consisting of 5.6 grams of ammonium persulfate dissolved in 147 grams of deionized water were added to the kettle and the temperature was set and maintained at 80°C. The remainder of the monomer solution was then fed to the reactor over a period of 225 minutes. Five minutes after the monomer feed was started, an initiator feed composed of 4.2 grams of ammonium persulfate dissolved in 107.8 grams of deionized water was started and fed to the reactor over a time period of 240 minutes. Fifteen minutes after the initiator feed was completed, a post initiator solution composed of 0.3 gram of ammonium persulfate and 0.3 gram of sodium

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metabisulfite dissolved in 49.4 grams of water was added over a time period of 30 minutes. After the final addition of reaction material, the aqueous emulsion of polymer was kept at the 80°C reaction temperature for an additional 30 minutes. Analysis indicated that the emulsion had a pH of 2.25, a Brookfield viscosity of 7.1 centipoise (LVT #1 at 60 rpm). There was a 96.1% conversion of monomer, polymer or solids content was 40.66%, and the polymer had a Mn of 10,800 and a Mw of 26,800 g/mole.

Preparation B

Preparation of an aqueous emulsion polymer

A monomer solution mixture composed of the compounds in Table 2 was prepared.

Table 2

<u>Monomer</u>	<u>Grams Used</u>	<u>Wt. % of Mixture</u>
Methyl methacrylate	450.0	44.2
Methyl methacrylate	450.0	44.2
Styrene	200.0	19.7
n-Butyl methacrylate	202.7	19.9
Methacrylic acid	10.2	1.0
2-Hydroxyethyl acrylate	137.3	13.5
n-Butylmercaptopropionate	17.2	1.7

The aqueous emulsion polymer was prepared in the same manner as that used for Preparation A. There was a 100% conversion of monomer, polymer or solids content was 43%.

Example 1

Modification of Preparation B aqueous emulsion

To a three-necked, round-bottomed glass reaction flask equipped with a condenser, mechanical stirrer, and thermometer, 50

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grams of Preparation B aqueous emulsion were added. While stirring the emulsion, 0.5 gram of Surfactant 2 were added and the pH of the emulsion was adjusted to 7.7 with an aqueous triethylamine solution made up of 10 grams deionized water, 3.84 grams triethylamine, and 0.10 gram of Surfactant 2. The mixture was stirred for 30 minutes at room temperature, and then 3.87 grams of 2-isocyanatoethyl methacrylate were added. The reactants were then stirred for 30 minutes before adding 0.5 gram of Surfactant 2. The mixture was stirred for 22 hours at room temperature and then stored for future use. Solids content of the ethylenically unsaturated aqueous emulsion was 46.15%.

Example 2 and Control I

Evaluation of aqueous emulsion polymers

To 100 weight parts of the Example 1 product and to 100 weight parts of Preparation B product, 5 weight parts of t-butyl peroxybenzoate were added per 100 parts of the respective products. The ingredients were stirred and then oven cured in aluminum dishes at the indicated temperatures for 30 minutes. After the cured products cooled to room temperature, 50 milligram samples of each were removed from the pans and gel fraction was determined as a percentage and is given in Table 3. The results indicate an increase in the amount of insolubilization with the aqueous emulsion polymer of Example 1 in comparison with the starting material, unmodified aqueous emulsion polymer of Control I, indicating improved chemical resistance.

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Table 3

<u>Examples</u>	<u>Percent Gel Fraction</u> <u>Temperature</u>		
	<u>120°C</u>	<u>160°C</u>	<u>180°C</u>
Example 2	28	49	50
Control I	2	1	0

Preparation CPreparation of an aqueous emulsion polymer

A monomer solution mixture composed of the compounds in Table 4 was prepared.

Table 4

<u>Monomer</u>	<u>Grams Used</u>	<u>Wt. % of Mixture</u>
Methyl methacrylate	299.5	29.6
Styrene	200.0	19.8
n-Butyl methacrylate	450.0	44.5
Methacrylic acid	10.0	1.0
2-Hydroxyethyl acrylate	40.5	4.0
Surfactant I	11.2	1.1

To the reactor described in Preparation A, 1,100 grams of deionized water, 2.1 grams of Surfactant I, and 5.1 grams of ammonium persulfate were charged. While stirring the contents at 300 rpm, the temperature of the mixture was increased to 80°C and a feed of the monomer mixture was begun. The monomer mixture was fed to the reactor over a 241 minute period, and 15 minutes after completion of the feed, a post-initiator solution consisting of 0.3 gram of ammonium persulfate and 0.3 gram of sodium metabisulfite

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dissolved in 49.4 grams of water was added. The aqueous emulsion was maintained at 80°C for 15 minutes after the addition, cooled to room temperature, and 20 grams of Surfactant 2 were added, stirred for an additional 15 minutes, and then filtered. A total of 2146 grams of emulsion was obtained with a solids content of 46%. The copolymer had a number-average molecular weight of 73,500 and a weight-average molecular weight of 467,000 as measured by gel permeation chromatograph using polystyrene standards.

Example 3

Modification of Preparation C aqueous emulsion

To a four-necked, glass resin kettle equipped with a condenser, mechanical stirrer, and thermometer, 1,000 grams of Preparation C aqueous emulsion were added. While stirring the emulsion, the pH of the emulsion was adjusted to 7.2 with a 14% aqueous solution of ammonium hydroxide. Stirring was continued at room temperature and 16.1 grams of 1-(1-isocyanato-1-methyl ethyl)-4-(1-methyl ethenyl) benzene (m-TMI). Analysis indicated the presence of isocyanate absorption at 2260 cm⁻¹ in the mixture. The mixture was then heated to 80°C and kept at this temperature for 6 hours. Infrared analysis indicated only 2.8% of the TMI remained. After standing at room temperature for 3 days, infrared analysis indicated only 1.2% of the TMI remained. The emulsion was filtered and a total of 735 grams of the aqueous emulsion polymer, 54.42% solids, was obtained.

Example 4

Modification of Preparation C aqueous emulsion

The same equipment, procedure, and ingredients of Example 3 were used except 39.1 grams of 1-(1-isocyanato-1-methyl ethyl)-4-(1-methyl ethenyl) benzene, m-TMI were used. After 5.5 hours at 80°C, infrared analysis indicated 6.2% of the TMI remained. Heating at temperature was continued for an additional 2.5 hours. The emulsion was cooled to room temperature, 5.0 grams of Foamaster® VL (Henkel) were added while stirring, and then filtered.

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A total of 797 grams of the aqueous emulsion polymer, 49.35% solids, was obtained.

Controls II - VIII

Evaluation of aqueous emulsion polymers

To 6.31 grams of Preparation C aqueous emulsion, 0.55 gram of the indicated filming aid were added. The mixtures were stirred for at least 30 minutes and then coated onto Bonderite cold-rolled steel panels by the draw down technique. The ten-mil wet films were allowed to stand under ambient conditions for two day after which period of time samples of approximately 50 milligrams were used to determine gel fraction as a percentage. Each gel fraction value is an average of four measurements. Dry or cured film thickness varied from 1.0 to 1.5 mils. From the low gel fractions obtained after two days, Table 5, under ambient curing, it is apparent that very little if any insolublization or crosslinking took place.

Table 5

Control Examples

<u>Ingredients, grams</u>	<u>II</u>	<u>III</u>	<u>IV</u>	<u>V</u>	<u>VI</u>	<u>VII</u>	<u>VIII</u>
Preparation C	6.31	6.31	6.31	6.31	6.31	6.31	6.31
Disopropyladipate	---	0.55	---	---	---	---	---
Divinyladipate	---	---	0.55	---	---	---	---
Trimethylolpropane triacrylate	---	---	---	0.55	---	---	---
Diallylphthalate	---	---	---	---	0.55	---	---
Diallylmalate	---	---	---	---	---	0.55	---
Ethylene glycol dimethacrylate	---	---	---	---	---	---	0.55

Cured Film Properties

Gel Fraction, %	3 / 1	6 / 3	5 / 9	6 / 6	2 / 1	3 / 1	3 / 2
Impact, Forward/Reverse	35/8	>84/50	>84/84	>84/15	80/80	75/50	>84/84
Gloss, 20°/60°	36/62	24/74	25/75	25/74	19/67	22/72	24/75
Yellowness Index	17	17	24	23	24	29	23
Definition of Image, DOI	0	0	0	0	0	0	0
Crosshatch Adhesion	4B	5B	4B	4B	4B	3B	3B

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Examples 5-12

Evaluation of aqueous emulsion polymers

The ingredients given in Table 6 were combined and the mixtures were stirred for 30 minutes. The formulations were coated onto Bonderite cold-rolled steel panels with a draw-down rod to yield 10-mil wet coatings which were allowed to remain under room temperature ambient conditions for two days. They were then evaluated and the properties of the cured coatings are given in Table 6. Each gel fraction value is an average of four measurements. Dry or cured film thickness varied from 1.0 to 1.5 mils. In comparison with Controls II to VIII above, the gel fraction is greater and the gloss, Definition of Image, Yellowing Index, and adhesion of these examples is improved over that of the controls.

Table 6

Ingredients, grams	Examples											
	5	6	7	8	9	10	11	12				
Example 3 polymer	6.31	---	---	---	---	---	---	---				
Example 4 polymer	---	6.31	6.31	6.31	6.31	6.31	6.31	6.31				
Diisopropyladipate	---	---	0.55	---	---	---	---	---				
Divinyladipate	---	---	---	0.55	---	---	---	---				
Trimethylolpropane triacrylate	---	---	---	---	0.55	---	---	---				
Diallylphthalate	---	---	---	---	---	0.55	---	---				
Diallylmalate	---	---	---	---	---	---	0.55	---				
Ethylene glycol dimethacrylate	---	---	---	---	---	---	---	0.55				

Cured Film Properties	Examples											
	5	6	7	8	9	10	11	12				
Gel Fraction, %	42/2	47/6	46/2	48/4	42/5	46/3	50/10	54/9				
Impact, Forward/Reverse	25/6	40/4	>84/60	>84/25	30/5	>84/10	>84/84	>84/35				
Gloss, 20°/60°	67/92	60/94	87/100	88/100	73/95	86/100	87/100	84/96				
Yellowness Index	2.5	2.2	3.5	3.2	2.8	3.2	3.1	2.9				
Definition of Image, DOI	19	22	28	30	24	32	30	33				
Crosshatch Adhesion	5B	4B	5B	5B	4B	5B	5B	5B				

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Examples 13 and 14 and Control IX

These examples and control describe and compare the scrub resistance of pigmented paints made from the control and ethylenically-unsaturated, nitrogen-containing aqueous emulsion prepared from the control. The pigment grind materials are conventional materials and commercially available as follows: Tamol® 681 (Rohm & Haas); AMP-95 (Angus Chemical); Triton® X-102 (Union Carbide Chemicals and Plastics Company Inc.); DeeFo® 495 (Ultra Additives); Ti-Pure® R-900 (DuPont); and Nuosept® 95 (Huls). To evaluate the scrub resistance, the following ingredients were combined and dispersed to form a pigment grind.

Table 7

<u>Pigment Grind Materials</u>	<u>Grams</u>
Water	10.00
Propylene glycol	60.00
Tamol® 681	7.86
AMP-95	2.00
Triton® X-102	1.00
DeeFo® 495	2.50
Titanium Dioxide, Ti-Pure® R-900	250.00
Nuosept® 95	3.00
Water	3.00
Total	339.36

The paint was prepared from the pigment grind by blending the following ingredients in what is termed in the art as a letdown procedure. The letdown ingredients are conventional materials and are commercially available as follows: Triton® Gr-7M (Union Carbide Chemicals and Plastics Company Inc.); DeeFo® 495 (Ultra Additives); and Acrysol® SCT-275 (Rohm & Haas).

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Table 8

<u>Letdown Ingredients</u>	<u>Grams</u>
Pigment grind	339.00
Water	50.00
Aqueous emulsion of Preparation C, Example 3, or Example 4*	480.00
Diallyl phthalate	17.76
Triton® Gr-7M	0.50
DeeFo® 495	2.50
Water	100.00
Propylene glycol	20.00
Acrysol® SCT-275	8.75
Water	27.99
Ammonia	2.0
Total	1,049.21

* When the aqueous emulsion of Preparation C was used, Control IX resulted; when the modified aqueous emulsion of Example 3 was used, Example 13 resulted; and when the modified aqueous emulsion of Example 4 was used, Example 14 resulted.

A seven-mil wet film of a commercial gloss alkyl paint (Glidden Alkyd Enamel 4554 green) was made on a Leneta scrub panel by the draw-down technique. The alkyd film was allowed to air dry for more than two days. Then a seven-mil wet draw down of the Control IX, Example 13, or Example 14 paint was drawdown over the aged commercial alkyd and allowed to air dry for three days. The dried or cured test control or example paint was cross hatched with a razor blade and submerged into water for 30 minutes. While the paint was still wet, the panel was placed on a Gardner scrub machine. Twenty grams of a 5% Lava soap slurry were added and a Nylon scrub brush (WG 2000 NB) was passed over the wet, crosshatched paint area.

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Water was added as needed to keep the paint film wet. The number of brushing cycles were noted for 10%, 50%, and 100% failure. The results are given in Table 9. The results show that the aqueous emulsion polymer products of Examples 13 and 14 have improved properties over the aqueous emulsion polymer of Control IX.

Table 2
Number of Scrubs to Cause Indicated Degree of Failure

Degree of Failure	Control IX	Example 13	Example 14
Initial Failure	1	6	1
10% Failure	2	39	9
50% Failure	--	96	14
100% Failure	8	238	54

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Preparation D**Preparation of a core and shell aqueous emulsion**

A glass reactor equipped with a stirrer, thermometer, nitrogen inlet and outlet, and feeding ports was charged with 986.43 grams of deionized water, 1.07 grams of Surfactant 1, and 1.43 grams of Surfactant 2. A nitrogen purge was started, and the contents of the reactor were heated to 80° C while stirring at 400 revolutions per minute (rpm). To form the core of the aqueous emulsion particles, after temperature was reached, 50 grams of Feed 1, Table 10, were added along with a mixture containing 3.0 grams of potassium persulfate dissolved in 147 grams of deionized water and stirred for 5 minutes.

Table 10**Feed 1. Aqueous Emulsion Polymer Core Feed**

<u>Monomer</u>	<u>Grams Used</u>	<u>Wt. % of Mixture</u>
Methyl methacrylate	400.0	49.55
Styrene	160.0	19.82
n-Butyl methacrylate	232.0	28.74
Methacrylic acid	0.80	0.10
Hydroxyethyl acrylate	9.71	1.20
Surfactant 1	2.4	0.30
Surfactant 2	2.4	0.30

Then, with the temperature maintained at 80° C, the remainder of Feed 1 was added over a 190 minute period. Immediately after Feed 1 was started, an initiator feed composed of 2.20 grams of potassium persulfate dissolved in 107.8 grams of deionized water was begun and continued over a 240 minute period. When Feed 1 was completed, Feed 2, Table 11 was started and added to the reactor over a 50 minute period.

Table 11
Feed 2. Aqueous Emulsion Polymer Shell Feed

<u>Monomer</u>	<u>Grams Used</u>	<u>Wt. % of Mixture</u>
Methyl methacrylate	70.0	31.0
Styrene	30.0	13.3
n-Butyl methacrylate	80.0	35.4
Methacrylic acid	20.0	8.9
Hydroxyethyl acrylate	24.7	10.9
Surfactant 1	0.60	0.27
Surfactant 2	0.60	0.27

Total time of addition for Feeds 1 and 2 was 240 minutes. After the reactants were added to the reactor, the aqueous emulsion was heated for 15 minutes at 80° C. The emulsion, which had a 42.9% total solids, was cooled and stored for future use.

Example 15
Modification of Preparation D aqueous emulsion

A glass reactor was equipped with a condenser, stirrer, and thermometer and charged with 400 grams of Preparation D emulsion. Then a mixture containing 1.00 gram allyl glycidyl ether, 10.11 grams of 1-(1-isocyanato-1-methyl ethyl)-3-(1-methyl ethenyl)benzene, m-TMI, and 0.055 gram Surfactant 1 were added in a dropwise manner to the stirring emulsion at room temperature. Then 10.1 grams of deionized water were added to adjust solids. The emulsion was stirred for 30 minutes at room temperature and then heated to 80°C and held there for 3 hours. The latex was cooled to room temperature and stored for future use. Total solids content was 43.2%. The latex gel fraction was 37.8%.

Although the invention has been illustrated by certain of the preceding examples, it is not to be construed as being limited thereby; but, rather, the invention encompasses the generic area as

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hereinbefore disclosed. Various modifications and embodiments can be made without departing from the spirit and scope thereof.

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Claims

1. A polymer having one or more pendant flexible side chains connected thereto, wherein said pendant flexible side chains contain ethylenic unsaturation and are connected to said polymer by a urethane linkage, said urethane linkage formed by the reaction of an ethylenically unsaturated isocyanate with a hydroxyl group on said polymer.

2. The polymer of claim 1 wherein the ethylenically unsaturated isocyanate is 2-isocyanatoethyl methacrylate, 1-(1-isocyanato-1-methyl ethyl)-4-(1-methyl ethenyl) benzene or mixtures thereof.

3. A process for preparing a polymer having one or more pendant flexible side chains connected thereto comprising:

- (a) preparing a precursor polymer having hydroxyl group functionality from one or more ethylenically unsaturated monomers;
- (b) post reacting the precursor polymer with one or more ethylenically unsaturated isocyanates; and
- (c) optionally recovering the step (b) polymer and redissolving it in an organic solvent.

4. The process of claim 3 wherein step (a) is carried out at a temperature of about 40°C to about 100°C and a pressure of about atmospheric to about 100 psig, and step (b) is carried out at a temperature of about 0°C to about 100°C and a pressure of about atmospheric to about 100 psig.

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5. The process of claim 3 in which at least 5% of the polymer precursor hydroxyl content is consumed in step (b), and in which said ethylenically unsaturated isocyanate is used in stoichiometric deficiency with respect to the hydroxyl group functionality in said polymer precursor, the isocyanate functionality being consumed in the process with the excess hydroxyl group functionality.

6. An ambient curable coating composition (and cured film prepared therefrom) comprising the polymer of claim 1, optionally a plasticizer, and optionally one or more drier salts.

7. A thermally curable coating composition (and cured film prepared therefrom) comprising the polymer of claim 1, an oxygen-producing compound, and optionally a plasticizer and/or one or more drier salts.

8. A radiation curable coating composition (and cured film prepared therefrom) comprising the polymer of claim 1, a photoinitiator, and one or more radiation-polymerizable unsaturated compounds.

9. A latex composition or an air drying and air curable latex coating composition comprising water and the polymer of claim 1.

10. A water-borne or solvent-borne composition comprising the polymer of claim 1.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 94/06990

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08G18/81 C08G18/62 G03F7/038

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C08G G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR,A,2 136 779 (BAYER) 22 December 1972 see claims 1,4-6 see page 3, line 7 - page 6, line 26 see page 7, line 1 - line 14 see page 8, line 22 - line 27 see examples 1,2 ---	1-8
X	FR,A,2 134 645 (AGFA-GEVAERT) 8 December 1972 see claims 1-6 see page 3, line 3 - line 34 see page 4, line 5 - line 26 see page 5, line 18 - line 30 see page 6, line 15 - line 28 see examples 1,2 --- -/--	1-6,8

☒ Further documents are listed in the continuation of box C.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 94/06990

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 259 726 (SIEMENS) 16 March 1988 see claims 1,3,4,6 see page 5, line 54 - page 6, line 7 see page 8, line 13 - line 23 ---	1,2,6-8
X	EP,A,0 206 158 (SIEMENS) 30 December 1986 see claims 1-4,6,9,10 see column 9, line 12 - column 10, line 20 see column 13, line 1 - line 16 ---	1,2,6-8
X	US,A,5 049 623 (W.A. DUPONT) 17 September 1991 see claims 1-7 see column 3, line 41 - column 4, line 30 -----	1-6,8

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Information on patent family members

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PCT/US 94/06990

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